Magnetic Doped Perovskite Oxides

Claiming of the Benefit of Provisional Patent
This non-provisional patent is applied to claim the benefit of the provisional application
under 35 U.S.C.119(e). The information of the corresponding provisional application is:
Title: Magnetic Doped Perovskite Oxides   Applicants: Yi-Qun Li, et al.
Application Number: 60/436,102   Filing Date: 12/20/2002   Confirmation No. 5953

Field of the Invention

This invention releases to provision of new compositions of metal oxide materials that
have ferromagnetic or ferrimagnetic properties and have resistivity in a range from
semiconducting to insulating.

Background of the Invention

Recent discovery of optically induced quantum coherent spin-state in semiconductors has
opened up a wide range of possibilities of spin-controlled devices, such as ultra-high
speed spin-controlled-optical switching and modulation, and quantum spin phase logic
devices. One of the major technical barriers to realize the implementation of these
devices is the proper spin injection contact materials that will effectively inject spin
polarized electrons into semiconductors. One approach is the development of room
temperature ferromagnetic semiconductors. Spin injection through a ferromagnetic
semiconductor heterostructure has been demonstrated. So far, there is no ferromagnetic
or ferromagnetic materials have Curie temperature higher than room temperature (300K)
and a resistivity of semiconductors. Most of ferromagnetic oxides are either metals or
insulators. (Ga,Mn)As is only ferromagnetic semiconductor but its Curie temperature is
as low as 120K. Some theoretical and experimental works indicate that (GaMn)N may
exhibit room temperature ferromagnetism. But, unfortunately, the experimental result of
Curie temperature of such material is only 250K. Several ferromagnetic metal oxides
such as $(La,M)MnO_3$ (M=Ca, Sr, Ba, Pb, ...), $Sr(M_{0.5}Mo_{0.5})O_3$ (M=Fe, Mn, Co, Cr,..)
have also been investigated for spin injection materials. However, these families of
ferromagnetic oxides behave as metals with a relative high conductivity rather than
semiconductors. Therefore, there is an urgent need to invent new materials that will
enable effective injection of nearly 100% spin polarized electrons into semiconductors
switched by low magnetic field at room temperature.

Summary of the Invention

These needs are met by the invention, which provides several groups of compound
semiconductor oxides in which spontaneous magnetization is existed with Curie
temperatures higher than room temperature (>300K) and their conductivity can be
controlled in a range from semiconducting to insulating.

. General chemical compositions for groups of oxide materials with simple perovskite
structures are $(A_{1-x}M_x)BO_3$, $(A_{1-x}M_x)(B'B'')O_3$ or $A(B_{1-x}M_x)O_3$, (where A can be 1+, 2+

and 3+ ions; B can be 5+, 4+, 3+ ions; B' and B" can be 2+, 3+, 4+, 5+ and 6+ ions, M is a magnetic ion dopant). Specific examples are $(A_{1-x}M_x)TiO_3$, $(A_{1-x}M_x)ZrO_3$, $(A_{1-x}M_x)SnO_3$, $(A_{1-x}B_x)HfO_3$, $La(Mo_{1-x}M_x)O_3$, $Sr(Ti_{1-x}M_x)O_3$ where A=Ca, Sr, Ba, Pb, Cd and M= Fe, Ni, Co, Mn <u>with 0<x<0.15</u> ~~(0.0202)~~.

Brief Description of the Drawings

Figure 1a, 1b, 1c, and 1d are theta-2 theta x-ray diffraction patterns for $(Ba_{0.94}Fe_{0.05})TiO_3$ $(Ba_{0.94}Co_{0.05})TiO_3$, $(Ba_{0.94}Ni_{0.05})TiO_3$, and $(Ba_{0.94}Fe_{0.05})ZrO_3$, respectively.

Figure 2 are plots of magnetization (μ_B/Fe) measured as a function of magnetic field at a temperature of 300K by SQUID magnetometer for a series of $(Ba_{1-x}Fe_x)TiO_3$ with x =0.01, 0.02, 0.03, 0.05, 0.07, and 0.1.

Figure 3 are plots of magnetization (μ_B/mol) measured as a function of magnetic field at a temperature of 300K by SQUID magnetometer for a series of $(Ba_{0.95}M_{0.05})TiO_3$ with M=Fe, Co, and Ni.

Figure 4 are plots of magnetization (μ_B/mol) measured as a function of magnetic field at a temperature of 300K by SQUID magnetometer for a series of $(Ca_{0.95}M_{0.05})TiO_3$ with M=Fe, Co, and Ni.

Figure 5 are plots of magnetization (μ_B/mol) measured as a function of magnetic field at a temperature of 300K by SQUID magnetometer for a series of $(Ba_{0.95}Fe_{0.05})BO_3$ with B=Ti, Zr, and Hf.

Figure 6 are plots of magnetization (μ_B/mol) measured as a function of magnetic field at a temperature of 300K by SQUID magnetometer for a series of $(Ca_{0.95}Fe_{0.05})BO_3$ with B=Ti, Zr, and Hf.

Figure 7 is a curve of magnetization as a function of temperature for $(Ba_{0.95}Fe_{0.05})TiO_3$ and $(Ca_{0.95}Fe_{0.05})TiO_3$ from 5K to 300K by SQUID magnetometer.

Figure 8 is a hysteresis loop of $(Ba_{0.94}Fe_{0.05})TiO_3$ and $(Ca_{0.94}Fe_{0.05})TiO_3$ measured at 5K and 300K by SQUID magnetometer.

Figure 9 is the (a) Magnetization vs Temperature, (b) hysteresis loop of $La(Mo_{0.25}Fe_{0.75})O_3$ at 300K measured using vibration vibrating samples magnetometer (VSM).

Figure 10 is the (a) Magnetization vs Temperature, (b) hysteresis loop of $Sr(Fe_{0.05}Ti_{0.95})O_3$ at 300K measured using vibration vibrating samples magnetometer (VSM).
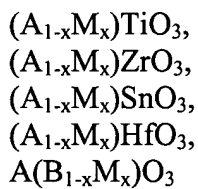
Description of Best Modes of the Invention

The invention includes general chemical compositions of the forms
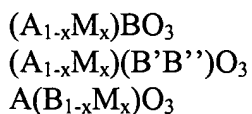
$(A_{1-x}M_x)BO_3$
$(A_{1-x}M_x)(B'B'')O_3$
$A(B_{1-x}M_x)O_3$

where A can be 1+, 2+ and 3+ ions; B can be 5+, 4+, 3+ ions; B' and B'' can be 2+ , 3+ 4+, 5+ and 6+ ions, M is a magnetic ion dopant such as Fe, Co, Ni and Mn.

Examples are:

$(A_{1-x}M_x)TiO_3,$
$(A_{1-x}M_x)ZrO_3,$
$(A_{1-x}M_x)SnO_3,$
$(A_{1-x}M_x)HfO_3,$
$A(B_{1-x}M_x)O_3$

where A=Ca, Sr, Ba, Pb, Cd, La, B=Mo, Ti, and M= Fe, Ni, Co, Mn with $0<x<0.15$. Representative bulk and thin film materials from these groups have been prepared by conventional ceramic powder process, ceramic solution process, and ion beam sputtering deposition, Laser ablation deposition respectively, for the choices of A= Ca and Ba, and, B=Ti and Mo, M = Fe, Co, and Ni.

Bulk samples of $(Ba_{1-x}Fe_x)TiO_3$ with x =0.01, 0.02, 0.03, 0.05, 0.07, and 0.1.
Bulk samples of $(Ca_{0.95}M_{0.05})TiO_3$ with M=Fe, Co, and Ni.
Bulk samples of $(Ba_{1-x}Fe_x)TiO_3$ with M=Fe, Co, and Ni.
Bulk samples of $(Ca_{0.95}Fe_{0.05})BO_3$ with B=Ti, Zr, and Hf.
Bulk samples of $(Ba_{0.95}Fe_{0.05})BO_3$ with B=Ti, Zr, and Hf.
Bulk sample of $La(Mo_{0.25}Fe_{0.75})O_3$.
Bulk sample of $Sr(Ti_{0.95}Fe_{0.05})O_3$.

Raw materials for preparing these samples are: Ba: $BaTiO_3$ or $BaCO_3$, Ca: CaO or $CaTiO_3$, Ti: TiO_2, Zr: ZrO_2, Hf: HfO_2, Fe: Fe_2O_3, Co: CoO, and Ni: NiO. La: La_2O_3, Mo: MoO_2, Sr: $SrCO_3$.

A method for producing these bulk ceramic materials comprises the following procedures:

1. Weighing the metal oxides according to the designed chemical stoichiometry.
2. Mixing these powders with solvent or water by ball milling for 20 minutes.
3. Drying the powder at 100°C for 1 hour.
4. The powder was calcined at 1100°C for 7 hours in air.
5. After ball milling, the dry powder was pressed into a cylinder pellet with a pressure of 100Mpa.
6. These pellets were fired at 1200-1350°C for 9-24 hours in N_2+H_2 or air atmosphere.

The samples of $(Ba_{1-x}Fe_x)O_2$ with X=0.01, 0.02, 0.03, 0.05, 0.07, and 0.1 exhibit magnetic properties with a increased saturation magnetization as X increases. The calculations of magnetization as contributed from each Fe ion are plotted in Figure 2. The sample with X from 0.01 to 0.05 has a similar magnetization per Fe ion with 2 Bohr magnetrons per Fe, which is about half of a pure Fe^{++} ion. Magnetization per Fe deceases as substitution of Fe to Ba increases for more than 5%. The result indicates that the solutability of Fe in A site of BaTiO3 is about 5% due to the large difference of ion size between Ba^{2++} and Fe^{2++}. The precipitation of either Fe_2O_3 or Fe_3O_4 has magnetization per Fe less than 2 Bohr.

Two series of bulk samples of $(Ca_{0.95}M_{0.05})TiO_3$ and $(Ba_{0.95}M_{0.05})TiO_3$ with M=Fe, Co, and Ni were prepared. Figure 3 and Figure 4 are magnetization curves of $(Ca_{0.95}M_{0.05})TiO_3$ and $(Ba_{0.95}M_{0.05})TiO_3$ with M=Fe, Co, and Ni, respectively. All of the samples shows ferromagnetic property. The saturation magnetization decreases in a sequence of Fe, Co and Ni which is consistent with the sequence for pure Fe2+, Co2+, and Ni2+ except Ni doped materials has relatively lower magnetization.

Two series of bulk samples of $(Ca_{0.95}F_{0.05})BO_3$ and $(Ba_{0.95}Fe_{0.05})BO_3$ with B=Ti, Zr, and Hf were prepared. Figure 5 and Figure 6 are magnetization curves of $(Ca_{0.95}Fe_{0.05})BO_3$ and $(Ba_{0.95}Fe_{0.05})BO_3$ with B=Ti, Zr, and Hf, respectively. All of the samples show ferromagnetic property. The saturation magnetization increases slightly in a sequence of Ti, Zr, and Hf at B sites for both $(Ca_{0.95}F_{0.05})BO_3$ and $(Ba_{0.95}Fe_{0.05})BO_3$.

Figure 7 is a curve of magnetization as a function of temperature for $(Ba_{0.95}Fe_{0.05})TiO_3$ and $(Ca_{0.95}Fe_{0.05})TiO_3$ from 5K to 300K. The Curie temperature is clearly higher than 300K. The complete hysteresis loops of $(Ba_{0.95}Fe_{0.05})TiO_3$ and $(Ca_{0.95}Fe_{0.05})TiO_3$ are measured at 5K and 300K as shown in Figure 8.

The coercive fields and remanent magnetization at temperatures of 5K and 300K for selected samples are listed in Table 1.

Table 1. Magnetic Properties of $(Ba_{0.95}Fe_{0.05})MO_3$ and $(Ca_{0.95}Fe_{0.05})MO_3$ (M=Ti, Zr, Hf)

	Hc(300K) (Oe)	Mr(300K)x10^{-4} μB/Mol	Hc(5K) (Oe)	Mr(5K) x10^{-4} μB/Mol
$(Ba_{0.95}Fe_{0.05})TiO_3$	16	3.84	26	7.55
$(Ca_{0.95}Fe_{0.05})TiO_3$	12	2.7	26	5.96
$(Ba_{0.95}Fe_{0.05})ZrO_3$	25	4.6	51	9.6
$(Ca_{0.95}Fe_{0.05})ZrO_3$	4.5	2.3	103	3.4
$(Ba_{0.95}Fe_{0.05})HfO_3$	20	4.5	51	11
$(Ca_{0.95}Fe_{0.05})HfO_3$	7	2.3	68	16

Figure 9(a) is a curve of magnetization as function of temperature for bulk sample $La(Mo_{0.25}Fe_{0.75})O_3$. The curie temperature of the sample is as high as 940K, and different that of the candidate impurity phase, Fe_3O_4 (850K), which strongly rules out the

existence of magnetic impurity Fe_3O_4 phase on the sample, and demonstrates the magnetic contribution of the doped Fe ions. The hysteresis loop of the sample measured at 300K using VSM is shown in Figure 9(b). The coercive fields and remanent magnetization at temperatures of 300K is 238Oe and 0.1589emu/g respectively. Figure 10 shows the magnetic properties of the Fe-doped $SrTiO_3$ with 5% Fe substitutingTi. The sample was annealed under reduced atmosphere (N_2+5%H_2). It is clear that the sample exhibits ferromagnetism at room temperature with large coercive field(117Oe, see Fig.10b) and a high curie temperature(610K, see Fig.10a)). The curie temperature of 530K can strongly evidence that the magnetism of the sample is from the doped Fe ion in the host lattices, rather than from the most possible impurity magnetic phase Fe_3O_4.